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THE STRUCTURE AND PROPERTIES OF POLYMERIC MATERIALS.(U)
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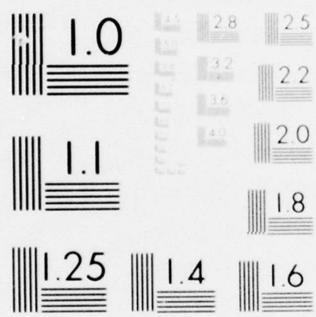
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FINAL SCIENTIFIC REPORT

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# THE STRUCTURE AND PROPERTIES OF POLYMERIC MATERIALS.

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# FINAL SCIENTIFIC REPORT

The preponderance of the results of the research investigations carried out under Grant No. 73-2441 covering the period from 15 August 1972 to 31 January 1977 have been published or are in press. Reprints and manuscripts covering these results have been submitted previously to AFOSR.

A total of thirty-five publications have been generated from this research. A publication list including all publications during the period of this report is appended. Those publications representing investigations supported in whole or in part by AFOSR are indicated by an asterisk. These papers have appeared, or will appear, in thirteen primary journals.

The following co-workers have been resident at Stanford for varying period of time, and have collaborated in the researches covered by this report:

Professor Wilma K. Olson, Rutgers University, New Brunswick, N.J.
Dr. G. D. Patterson, Bell Laboratories, Murray Hill, N. J.
Dr. R. T. Ingwall, Polaroid Corporation
Dr. H. Shih, duPont, Wilmington, Del.
Dr. C. J. Pickles, Lever Bros. Research, Liverpool, England
Prof. J. E. Mark, U. of Cincinnati, Cincinnati, Ohio
Dr. E. A. Czurylo, Warsaw University, Poland
Dr. S. Bluestone, California State U., Fresno, Ca.
Mr. L. C. DeBolt, Polytechnic Institute, New York
Dr. M. H. Liberman, U. S. Customs Laboratory, San Francisco, Ca.
Dr. P. R. Sundararajan, Xerox, Ontario, Canada
Dr. D. Y. Yoon, IBM, San Jose, Ca.
Professor Y. Tatara, Shizuoka University, Japan
Dr. U. W. Suter, Eidgenössische Technische Hochschule, Zürich, Switzerland

Dr. A. Abe, Showa Denko K.K., Tokyo, Japan

Dr. E. Saiz, University of Extrenadura, Badajuz, Spain

Dr. C. W. Carlson, duPont, Wilmington, Del.

Research as yet incomplete or awaiting preparation for publication is briefly summarized below:

Rubber Elasticity

It is now well established that the stress in a deformed rubber originates within the chains of the network. Interchain interactions contribute negligibly to the stress. The elastic properties of this broad class of materials (which includes nearly all linear polymers under suitable conditions) must therefore reflect the configurational characteristics of the polymer chains comprising the rubber network. In view of the copious interactions between neighboring chains in an amorphous polymer, this assertion may appear implausible. However, both theory and experiment provide abundant support. It is the objective of rubber elasticity theory therefore to compound the contributions of the individual chains additively, a task which is rendered difficult by the complexities of network structure and topology.

The connection between two traditional theoretical approaches to the treatment of rubber elasticity has been bridged by recent studies (see papers 46 and 49 of the publication list). One of these is the theory of "phantom" networks, developed originally by James and Guth, in which the integrity of the chains is ignored and the junctions (cross linkages) are allowed to seek their preferred positions without regard for the entanglements of chains that severely limit configurational rearrangements in real systems. The other follows the precepts of W. Kuhn elaborated by Wall, Treloar, Flory and Rehner and others, according to which the cross linkages are firmly embedded in their surroundings and hence must undergo ("affine") displacements in proportion to the macroscopic strain. The two theoretical approaches yield a stress-strain relationship of the same form, which for simple elongation is

$$f = \xi(kT/L_i)(\langle r^2\rangle_i/\langle r^2\rangle_0)(\alpha - \alpha^{-2})$$

where f is the force, $\alpha$ is the extension ratio relative to the length $L_i$ of the unstretched specimen at the prevailing volume, $\langle r^2\rangle_i$ is the mean-square length of a network chain in this rest state of length $L_i$, and $\langle r^2\rangle_0$ is the mean-square length for a free chain. For a phantom network $\xi$ is the cycle rank, i.e., the number of scissions required to reduce the network to a "tree." According to the theory for a network whose junctions (cross linkages) are subject to displacements that are "affine" in the strain, $\xi$ is the number of chains. For a tetrafunctional network (i.e., a cross-linked network) the number of chains is twice the cycle rank. Hence, in this case the respective theories differ by a factor of two. We suggest that the unswollen network at small deformations conforms approximately to the latter (affine) behavior, but that it approaches the phantom model at high elongations and/or high degrees of swelling. Hence, the numerical factor multiplying the equation above must be considered to decrease with strain and with dilution. This change may account for departures from the theoretical relationship.

Statistical Thermodynamics of Stiff Chains

The theory of order-disorder in systems of rigid extended polymer chains and of phase equilibria in such systems (Proc. Roy. Soc. London, A234, 73(1956)) has been adapted without difficulty to semiflexible chains consisting of rigid rod-like segments connected by flexible joints. The behavior predicted conforms closely to that of the system of disconnected rods of the length of the segments comprising the semi-flexible chain. Additionally, the equations have been elaborated to comprehend heterodisperse systems in which the lengths of the rods, or their axis ratios, are variable according to a specified distribution. Calculations on phase equilibria in such systems are difficult and are incomplete at this time.

Configurational Statistics of Vinyl Polymer Chains

Disubstituted vinyl polymers,

$$\left( -\overset{\displaystyle R}{\underset{\displaystyle R'}{\overset{|}{\underset{|}{C}}}} - CH_2 \right)_x - \quad ,$$

are of particular interest because of the rigidity imparted by the presence of two substituents, R and R'. These substituents introduce severe steric repulsions which occur in all conformations. We have calculated conformational energies for poly(methyl methacrylate) chains, in which $R = COOCH_3$ and $R' = CH_3$, and have deduced a relatively simple rotational isomeric state scheme for the analysis of its configurational statistics and configuration-dependent properties (see paper 24). The superficially simpler polyisobutylene chain in which $R' = R = CH_3$

presents difficulties of interpretation which thus far have resisted our efforts to bring theory into agreement with experiments. We propose to continue this investigation in order to establish a satisfactory basis for the interpretation of properties of this important polymer.

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A total of thirty-five publications have been generated from this research appearing in thirteen primary journals. The connection between two traditional theoretical approaches to the treatment of rubber elasticity has been bridged. One of these is the theory of "phantom" networks, developed originally by James and Guth, in which the integrity of the chains is ignored and the junctions (cross linkages) are allowed to seek their preferred positions without regard for the entanglements of chains that severely limit configurational rearrangements in real systems. The other follows the precepts of W. Kuhn elaborated by Wall,


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19. Abstract

Treloar, Flory and Rehner and others, according to which the cross linkages are firmly embedded in their surroundings and hence must undergo ("affine") displacements in proportion to the macroscopic strain. This research suggests that the unswollen network at small deformations conforms approximately to the affine behavior, but that it approaches the phantom model at high elongations and/or high degrees of swelling. Decreases with strain and dilution may account for departures from the theoretical relationship. The theory of order-disorder in systems of rigid extended polymer chains and of phase equilibria in such systems (Proc. Roy. Soc. London, A234, 73 (1956) has been adapted without difficulty to semiflexible chains consisting of rigid rod-like segments connected by flexible joints.